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14. ABSTRACT
Our research program has two interrelated components: the growth of GaN nanowires and the fabrication of electronic devices, including gas sensors, on these nanowires. A hydride vapor phase epitaxy (HVPE) reactor was designed and put in operation, and the processes for growing nanowires of GaN and AlN were developed, including n-core with p-shell structures, and, recently, GaN nanotubes. The nanowires were characterized morphologically (SEM), structurally (EBSD, XRD), and electrically using back-gated field-effect transistors fabricated using the

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Final report

Growth and Characterization of III-V Nitride Quantum Dots and Quantum Wires

Statement of the problems studied.

Nano wires and quantum dots offer new dimensions in semiconductor devices. Potentially superior material quality as well as the large surface to volume ratio and the fact that nature gives you the nano dimensions makes these structures fruitful subjects for research. In particular GaN and AlN and other related compounds offer unique electrical and also optical properties. We have concentrated on the growth of the nano wires, the characterization of their properties, and the demonstration of potentially useful device structures.

Growth

The first step was the installation of a chemical vapor deposition reactor. A hydride vapor phase epitaxy (HVPE) reactor was put in operation, and the processes for growing nanowires of GaN and AlN were developed, The nanowires were characterized morphologically and structurally.

Magnesium doping capability was also added to the reactor.
Twenty growth runs were done in order to develop recipe for GaN layer doping with Mg using the metalorganic source Cp2Mg (for p-type conductivity) with hole concentration range of 10^{16}- 10^{17} cm-3. The samples were processed and prepared for carrier concentration measurement by Hall method. These measurements showed a p-type conductivity on all processed samples with carrier concentrations in the range of 10^{16}- 10^{17} cm-3 depending on growth conditions (mostly on Cp2Mg flux).

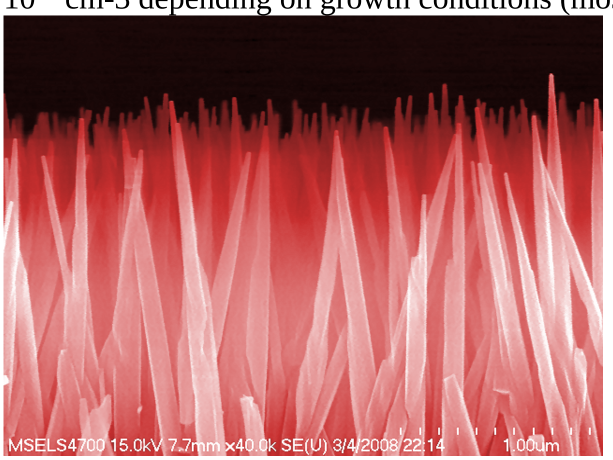


Fig. 1. AlN nano wires

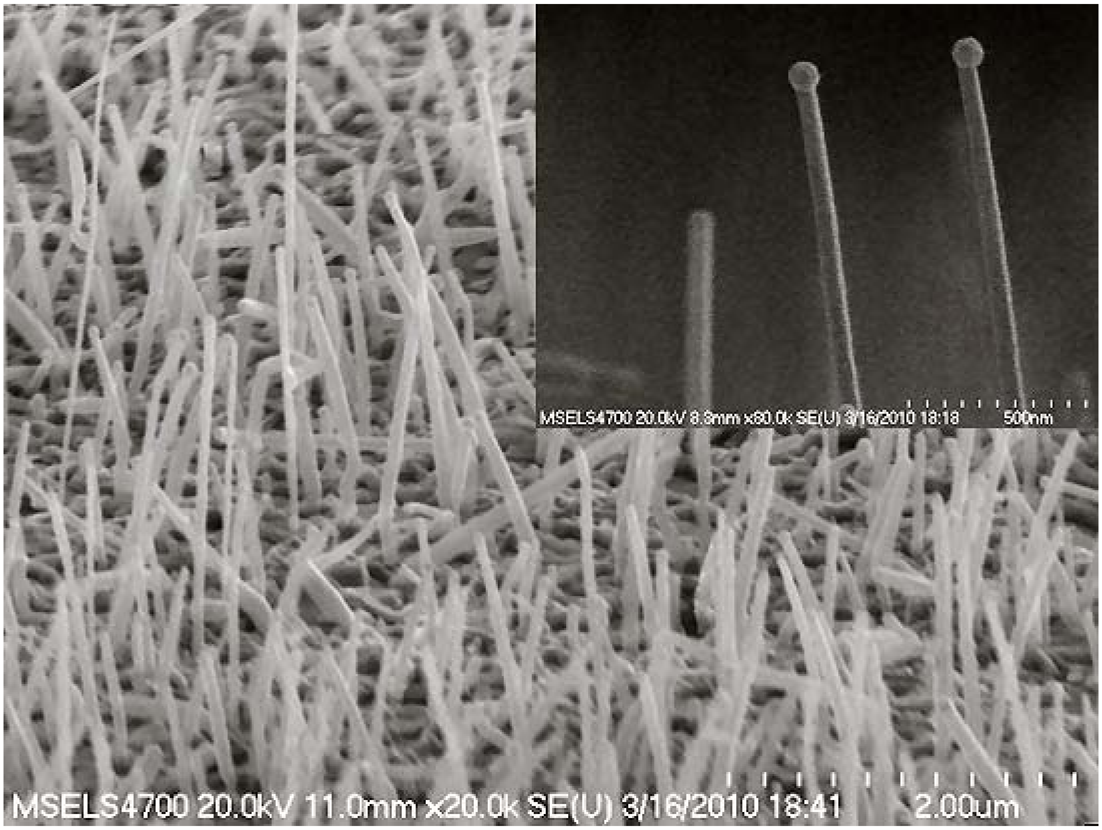


Fig. 2 SEM image of vertical GaN nanowire array fabricated on c-sapphire substrate utilizing HVPE method. Insert shows Au-droplets at the nanowire tips, which is indicative of the VLS (vapor-liquid-solid) growth mechanism.

We fabricated AlN and GaN nanowires on a variety of substrates: Si, sapphire, GaN/sapphire, and SiC and achieved vertical alignment of AlN needles on 1" diameter SiC substrates. See Fig.1 and Fig. 2. As-grown nanowires were characterized morphologically (SEM), and structurally (EBSD, XRD, TEM). XRD pole figures confirmed epitaxial relationship between AlN nanowires and SiC substrate. TEM on AlN nanowires revealed presence of occasional stacking faults This is the first demonstration of large-scale fabrication of well-aligned AlN nanostructures using commercial HVPE process. We presented initial results at the International conference in St-Petersburg, Russia (June 20-22, 2008), and we presented a talk to Bi-annual International Workshop on Nitride Semiconductors held in Switzerland (Oct. 6-10, 2008)

We optimized the recipe for the AlN buffer-on-Silicon for the subsequent growth of GaN and AlN Nanowires. The AlN buffer was successfully developed with low surface roughness and good crystal quality. Preparation procedure (ex-situ cleaning and etching) for Silicon substrate for HVPE growth processes was developed Optimization of AlN buffer-on-Silicon recipe for the subsequent growth of GaN and AlN Nanowires. AlN

buffer was successfully optimized in terms of surface roughness and crystal quality. Preparation procedure (ex-situ cleaning and etching) for Silicon substrate for HVPE growth processes was developed.

We performed overgrowth of P type GaN nanowire with an n-type shell and measured electrical and optical characteristics of the pn junction. Diode characteristics were observed electrically but so far no light emission was observed.. We found that the challenge of overgrowing an N shell on the P type wire is that the quality of the junction is poor. We performed growth on planar substrates to study and optimize the process. GaN p/n homojunction films were grown on sapphire. Electroluminescence from GaN p/n thin-film junction on sapphire was achieved. This recipe was then used for the growth of p-GaN shell on MBE grown n-GaN NWs.

Growth of GaN nano wire (NW) using different catalysts and growth initiations was investigated. Ni layer with a thickness of 1 nm was found as optimal catalyst for sapphire substrate. Initial high temperature nitridation of Ni catalyst using NH3 was found helpful to the growth of GaN nano wires with relatively low density. In the case of Si substrate with 111 orientation Au was found as optimal catalyst, Ni was found not to be acceptable as catalyst in the case of Si because growth did not occur.

Several samples with n-type GaN NW coated with SOG (spin-on-glass) were received from NIST at Boulder. The idea was to cover entire NW with SOG and etch SOG at the end of NW to expose NW for subsequent deposition of p-GaN shell in our HVPE reactor. Special holder was designed in order to be able to load samples in small sizes with up-side-down geometry. Many runs for further optimization of AlN buffer on 111 Si were done. It was found that miscut of 111 Si towards to 110 orientation allows to obtain AlN buffer of much better quality in terms of crystal structure and layer smoothness.

An exciting recent development is a discovery that we could grow GaN nano tubes. They are grown by using a core nano wire of InN, overgrowing withGaN, and then dissolving the InN. See Fig.3.

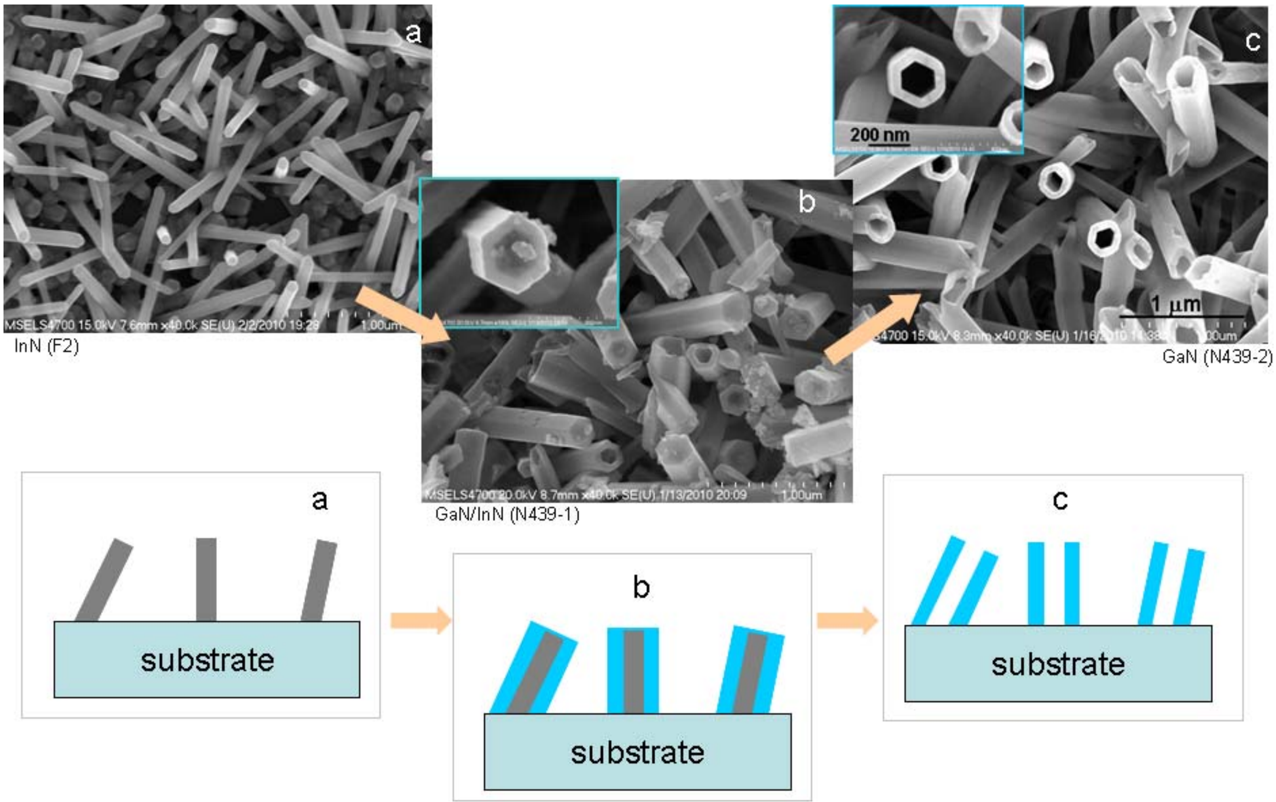


Fig 3. GaN nanotubes fabricated by “nano-casting” GaN shells over InN nanowires followed by InN core etching:

a) Initial set of InN nanorods, b) InN/GaN core/shell structures; c) GaN nanotubes after InN removal

Nanowire devices

Various electronic devices were fabricated on the nanowires both to exploit the unique characteristics of the nanowires grown as part of our program and also to further characterize their electrical properties.

Field effect transistors

One of the challenges of using nano wires in any practical application is to align them in some useful fashion on the planar substrate. We have used dielectrophoresis to align nano wires originally grown by molecular beam epitaxy at NIST-Boulder, Colorado. As shown in Fig. 4 the nano wires are floating in the solvent in which there are electrodes with an alternating signal applied to them. The nano wires are attracted to these electrodes, but once one nano wire lands on the electrodes others are no longer attracted because the electric field is shorted out. After the nano wires have been located between two electrodes a gate structure can be constructed as shown schematically to surround the nano wire completely to produce a transistor. Fig. 5 shows a transistor characteristic and the nano wire alligned between two electrodes using electrophoresis. We have fabricated a mask with multiple electrodes so that multiple nano wires can be aligned on the same substrate. After the alignment most of the electrode metal can be etched away thus

leaving room for circuitry. Another challenge in all of the device fabrication is contacts. We have developed processing techniques including metal contact schemes and annealing schedules for realization of p-type GaN nanowire based field-effect devices. This will enable us to make complimentary sensor architecture (with both n- and p-type nanowire devices on the same chip).

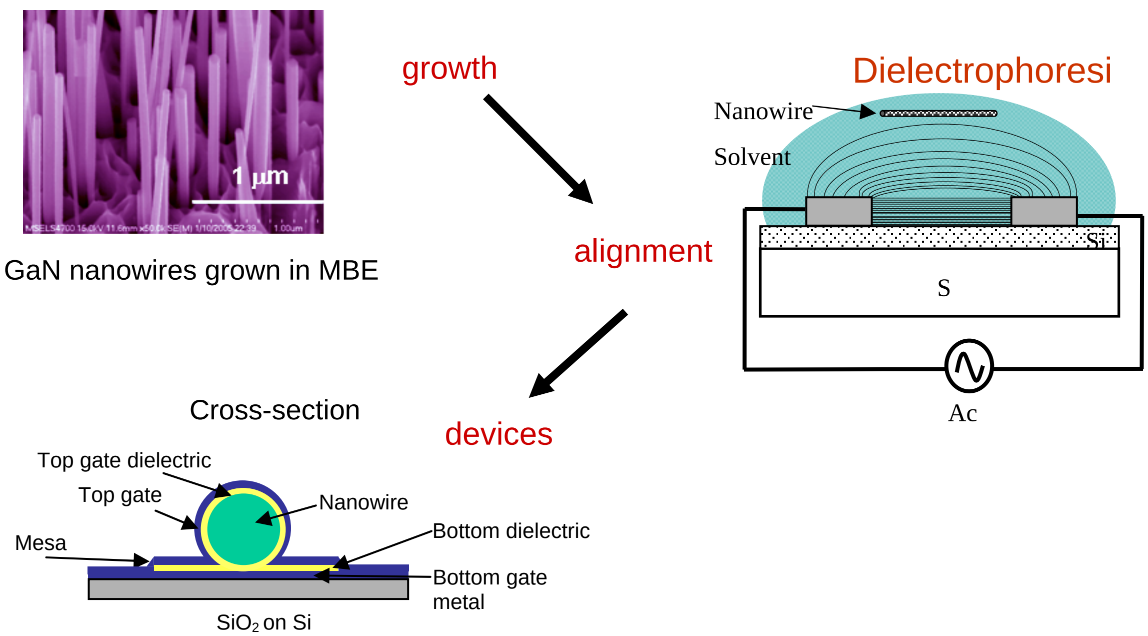


Fig. 4. Shows the nano wires of GaN, the alignment process, and a schematic of the type of transistor we have produced.

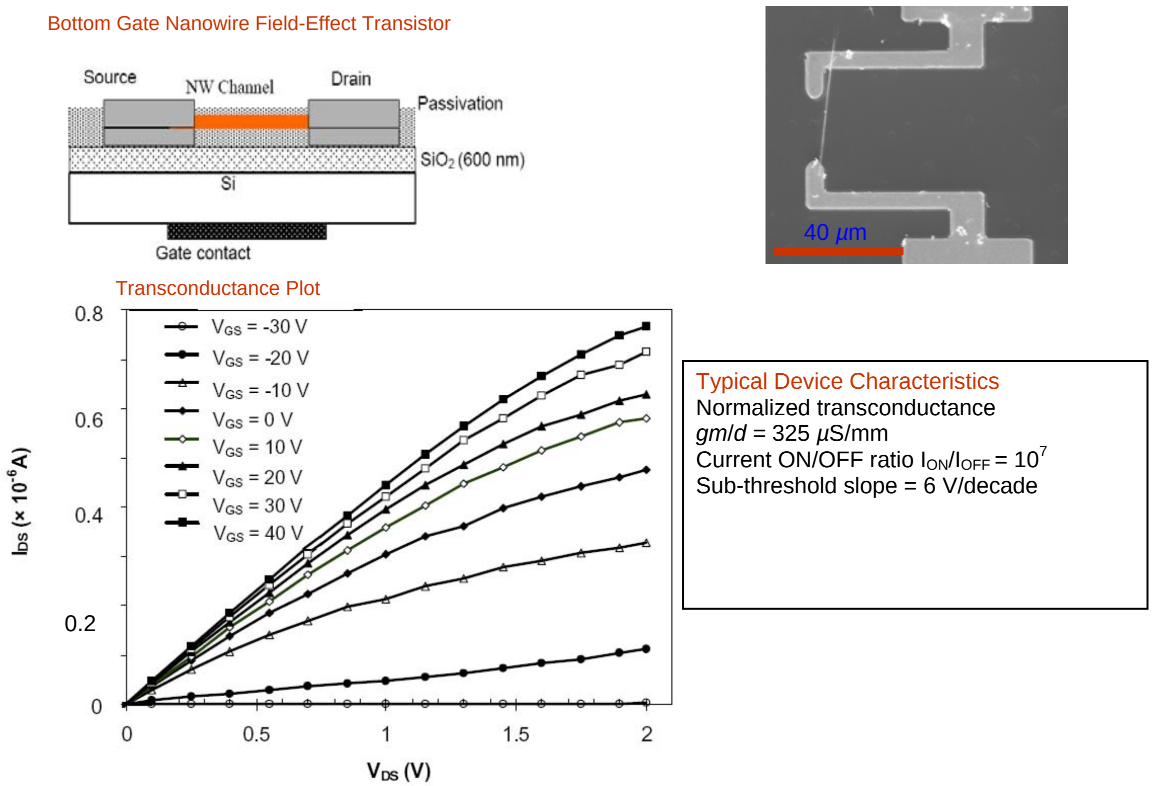
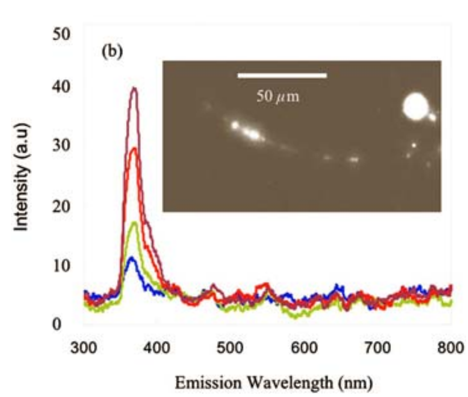


Fig. 5. SEM image of the nano wire aligned between two electrodes using electrophoresis, top right. Top left, schematic of the structure used to make a transistor with the bottom substrate as the gate. This structure is suitable for sensing. Bottom figure shows the transistor characteristics with a very high on/off ratio.

Light emitting diodes

GaN nanoscale light emitting diodes were constructed using n type GaN nano wires on p type GaN substrate. The devices were made using electric field assistant alignment for placing the nano wire on a p-type GaN thin-film thus forming a homojunction. Light emission at a wavelength of 365 nm was observed with a bandwidth of 25 nm. See figure 6. Light is preferentially emitted from specific points along the nano wire, where the contact between the nano wire and the substrate forms the best PN junction.

Fig. 6. The emission spectrum of the nanowire diode. The inset shows the nano wire and the points from which emission occurs. The blue, green, red, and violet curves represent emission recorded with injection currents of 35, 55, 65, and 75 microamps respectively.



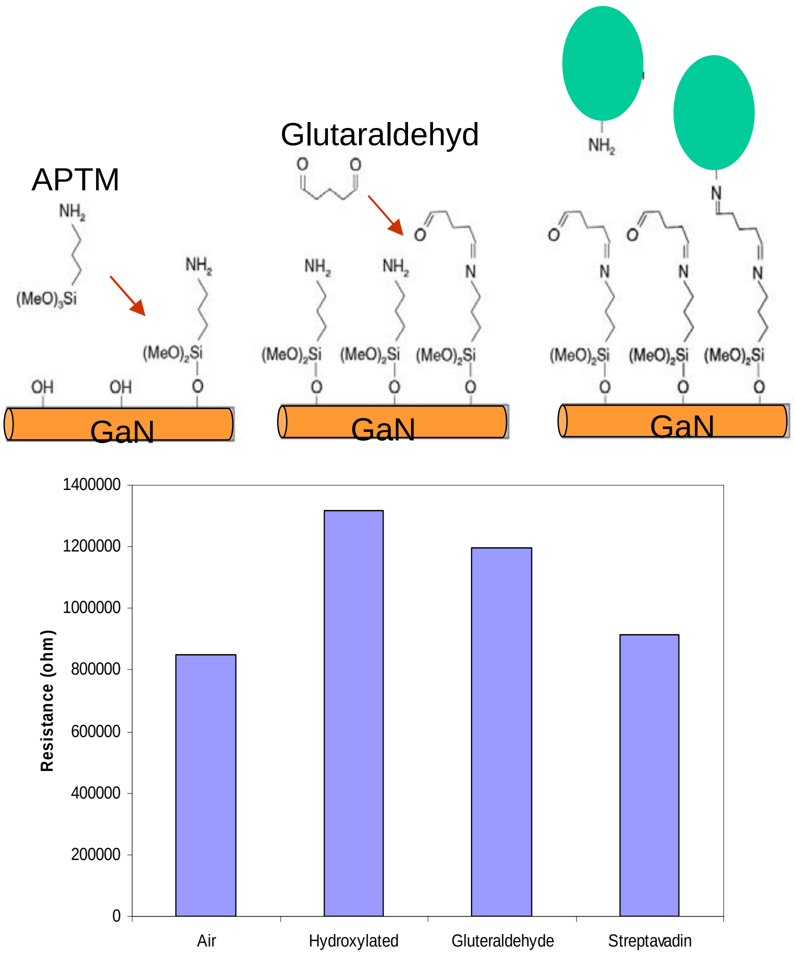


Fig. 7. A schematic of the attachment of molecules in the functionalization of the GaN nano wire, and in the deep connection of the streptavidin protein.

2. We have developed processing techniques including metal contact schemes and annealing schedules for realization of p-type GaN nanowire based field-effect devices. This will enable us to make complimentary sensor architecture (with both n- and p-type nanowire devices on the same chip).

Sensors

The main reason nano wires are potentially useful as sensors is the large surface to volume ratio. Thus small changes in the surface of the semiconductor nano wire, such as

changing the depletion width, will have a larger effect on electrical properties than it would in a bulk device. Three types of sensors were demonstrated: uncoated GaN nano wire, a nano wire with the surface functionalized, and the nano wire coated with nano dots of titanium oxide. The uncoated wire showed a change of 13% in conductivity due to 50 ppm of carbon monoxide in air. The nano wire that was functionalized with glutaraldehyde showed that 25% decrease in resistance when exposed to streptavadin. See Fig. 7. Nano wires were also fabricated on which particles, (nano dots), of titanium oxide were produced by sputtering a very thin film. These nano wires were able to detect ethanol at 100 ppm in air at room temperature with 25 microWatts operating power. Chloroform eas also similarlly detected. Photomodulation of the chemical sensitivity in these structures has been demonstrated. In other words, these GaN nanowire/TiO2 nanocluster hybrid sensors could sense 100 ppm of ethanol only when they are illuminated with 300-400 nm light. These sensors are completely refreshable and the refresh time is about 2 seconds.

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We have presented a summary of our most important advances in the gross of nano wires, in the understanding of their properties, in the fabrication of devices, including LEDs and sensors. A more detailed account of the work is found in the seven papers published in highly respected, peer-reviewed journals.